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Synthesis of Poly(p-[α-(N-t-butylnitronyl)]styrene) and Its Reactivity with Nitrogen Dioxide

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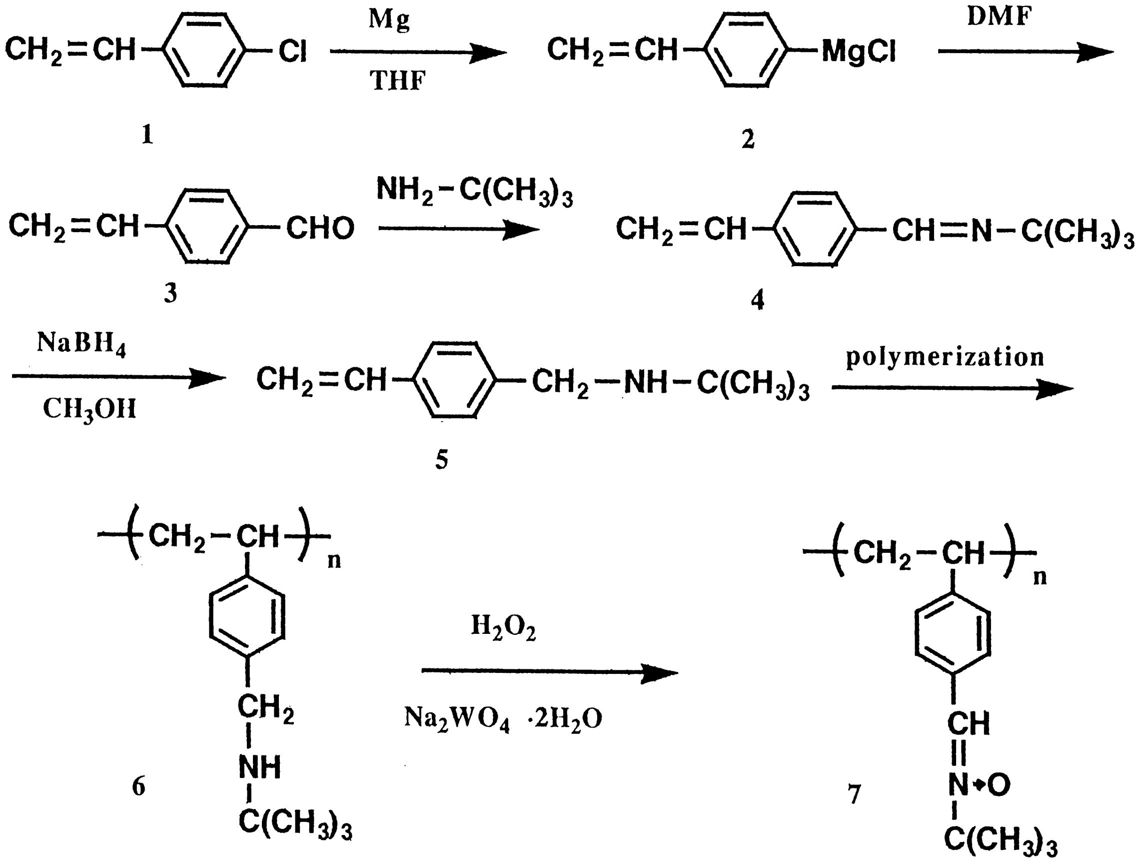
Poly(p-[α-(N-t-butylnitronyl)]styrene) (polyPBN) has been prepared by using p-chlorostyrene as a starting material. The reaction of polyPBN with nitrogen dioxide (NO_2) and its efficiency for radical trapping were studied. The stability of NO_2 adduct of polyPBN and operational simplicity to recover polyPBN showed that polyPBN is applicable to the removal of NO_2 in atmosphere.

It has been reported that phenyl-N-t-butylnitrone (PBN), which is widely used to detect short-lived free radicals, reacts with nitrogen dioxide (NO_2) in solution to give benzoyl-t-butyl nitroxyl.$^{1)}$ Our group has recently found the formation of a white solid adduct when a stream of NO_2 was passed through a hexane solution of PBN. The white solid adduct thus obtained can be hydrolyzed liberating NO_3^- and regenerating PBN quantitatively.$^{2)}$ Though our experimental results suggest that PBN is usable as a regent for NO_2 analysis or as a scavenger for NO_2 in atmosphere, there are several disadvantages for using PBN itself as a spin trap in actual environmental analysis. The NO_2 adduct is rather unstable and degrades gradually into a paramagnetic substance. A procedure to recover PBN from the NO_2 adduct is laborious and cautious handling is required. In order to overcome these disadvantages, we attempted the synthesis of a vinyl polymer of PBN in which the nitrone moiety in the side chain could be used to capture NO_2 reversibly. Polymer supported PBN can be expected to acquire several new properties advantageous to use for trapping NO_2 or free radical. It can be separated easily from the solution and should be convenient to be regenerated by the treatment with water.

In this communication, we wish to report the synthesis of poly(p-[α-(N-t-butylnitronyl)]styrene) and its reactivity with NO_2.

Because PBN has the ability to trap free radicals, vinyl polymer of

PBN cannot be obtained with conventional radical polymerization. Our synthetic route to polyPBN is shown in Scheme 1.



Scheme 1.

p-Chlorostyrene (1) was used as a starting material for the synthesis. p-Formylstyrene (3) was synthesized by the reaction of N,N-dimethylformamide (DMF) with p-vinylphenylmagnesium chloride (2), which was prepared by adding the solution of p-chlorostyrene to magnesium under nitrogen.[3] The next step in the reaction scheme was the condensation of p-formylstyrene with an excess of t-butylamine. The reaction was carried out by heating the mixture in benzene for three hours at 60 °C in the presence of a molecular sieve. Reduction of N-(p-vinylbenzylidene)-t-butylamine (4) was accomplished by the addition of $NaBH_4$ to its MeOH solution at room temperature, followed by heating the mixture for 15 min at 60 °C. N-t-Butyl-p-vinylbenzylamine (5) synthesized by this method was polymerized smoothly in the presence of AIBN at 70 °C under nitrogen. Obtained polymer (6) was easily soluble in benzene and dichloromethane. PolyPBN (7) was prepared by the oxidation of poly(p-[α-(N-t-butylamine)]styrene) with hydrogen peroxide in the presence of metal catalyst ($Na_2WO_4 \cdot 2H_2O$) at room temperature.[4]

In search for the possibility to use polyPBN as a reagent for environmental analysis, the reaction of polyPBN with NO_2 was carried out by passing NO_2 through a glass tube packed with polyPBN powder for 30 min. An IR spectrum of the polyPBN after reaction (KBr pellet) showed absorptions at 1620 and 1390 cm^{-1} characteristic of nitrate ester. These data indicated that the reaction product was a nitrate of polyPBN formed by the addition NO_3 to polyPBN as found in the experiment of PBN. NO_3 could be generated by the dissociative disproportionation of dinitrogen tetroxide which is in equilibrium with NO_2. This nitrate adduct regenerated polyPBN easily by washing the adduct with water and filtration. As the polyPBN adduct is almost insoluble in water, a prolonged treatment with water becomes necessary. After stirring the adduct in water for about one hour at room temperature, drastic decrease in the intensities of the nitrate absorptions was observed for the recovered polymer. In addition, NO_3^- and NO_2^- ions could be detected by brucine/concentrated sulfuric acid test and the Griess-Romijn test. These experimental results suggested that most of polyPBN adducts were converted to original polyPBN by washing with water. It is an intriguing aspect that polyPBN can react with NO_2 to form adduct in solid state. White solid adduct was observed when the PBN was reacted with NO_2 only in solution such as n-hexane. The increased reactivity of polyPBN towards NO_2 in solid state may be due to the microporous structure of polyPBN. When NO_2 gas is passing through polyPBN, the molecule must go through pores in the polymer structure and the probability to encounter with the nitrone moiety will increase to generate the adduct with NO_2. The properties of the NO_2 adducts of polyPBN and PBN are summarized in Table 1.

Table 1. The Properties of NO_2 Adducts of PolyPBN and PBN

	polyPBN	PBN
Reactivity with NO_2[a)]	Reactive	Unreactive
Stability	Stable	Unstable
IR spectra[b)] (NO_2)	1620 cm^{-1}, 1390 cm^{-1}	1638 cm^{-1}, 1370 cm^{-1}
Process to recover spin trap	Simple	Laborious

a) In solid state. b) KBr pellet.

In conclusion, polyPBN can react with NO_2 in solid state efficiently and be recovered from its adduct by water treatment. This reaction may become an application to the removal of NO_2 in atmosphere because of its operational simplicity.

As polyPBN is expected to be useful to capture free radicals both in solution and in atmosphere, we carried out the spin trapping experiments of polyPBN . The reaction was performed by heating the xylene solution of polyPBN and α,α-azobisisobtyronitrile (AIBN) at 120 °C for 4 min.$^{5)}$ After reaction, the solution was quenched and degassed with nitrogen for 5 min before measuring ESR spectra. It is concluded from ESR spectra of the polyPBN adduct that polyPBN can trap 2-cyano-2-propyl radical. However, polyPBN adduct showed weaker intensity than that of PBN adduct and did not give a characteristic doublet of triplets signal pattern which was observed in the PBN adduct. Weaker signal intensity suggests lower reactivity of polyPBN towards radical trapping. The polymer side chain may prevent the attack of the bulky radical to nitrone moiety. Though the splittings due to β-hydrogen were obscured to a great extent, this can be assigned to the polyPBN adduct. The polymeric spin adduct is separable easily from the solution and has a potential use for the analysis of free radicals. In order to investigate the stability and ESR spectra of radical adducts of polyPBN, methyl radical adduct of polyPBN was synthesized by the reaction of polyPBN with methyllithium followed by the oxidation with molecular oxygen.$^{6)}$ ESR spectrum of methyl adduct of polyPBN showed the same doublet of triplets hyperfine splitting pattern as that observed with the monomeric PBN adduct. However, the signal of polyPBN adduct was not so intense as that of the monomeric PBN adduct. Judging from their ESR spectra measured at regular intervals, the methyl and 2-cyano-2-propyl adducts of polyPBN can be preserved without change for a few days at room temperature.

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